

Transesterification of palm cooking oil using barium-containing titanates and their sodium doped derivatives

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Abstract BaTiO₃, Ba₂NiTi₅O₁₃ and their Na-doped analogues were successfully synthesized via sol–gel and calcination methods. The surface properties of the prepared catalysts were characterized by scanning electron microscopy and nitrogen adsorption–desorption analysis while the basicity was determined by benzoic acid titration. The catalytic activity of the Ba-based catalysts was verified in transesterification of palm cooking oil with methanol. The optimization study was conducted by varying the oil: methanol ratio, catalyst loading, reaction temperature and duration. The highest methyl ester (ME) yield was ~95% for 5 wt/v% Na-Ba₂NiTi₅O₁₃ at a methanol to oil ratio of 12:1 at 150 °C for 2 h.

Keywords Transesterification · BaTiO₃ · Ba₂NiTi₅O₁₃ · Sodium-doped · Catalyst

Introduction

Biodiesel has attracted interest as a promising energy source to substitute the drastically depleted fossil fuels in recent decades [1]. The main content in biodiesel is fatty acid methyl ester (FAME), which is an environmentally friendly fuel with clean burn, easily made, biodegradable, non-toxic and free of sulfur and aromatic compounds [2]. Transesterification reaction is the most common method to convert vegetable oils or animal fat into FAMEs using methanol in the presence of suitable catalyst. Generally,

heterogeneous catalysts are preferred over homogenous catalysts as it provides advantages such as simple separation process, good reusability and saponification prevention [3, 4].

Metal oxides have been extensively studied as heterogeneous base catalysts in transesterification. The presence of $M^{\delta+}-O^{\delta-}$ ion pairs in these oxides produces basic sites that are believed to be actively involved in the transesterification reaction [5]. Several attempts have been employed to further improve their catalytic properties and stability, such as doping [6, 7], immobilizing or supporting [8] and mixed oxide systems [9, 10]. For example, Mukenga et al. [8] have shown that the oil conversion for TiO₂ supported ZnO is higher than unsupported ZnO catalyst. Mar and Somsok [6] showed that the catalytic activity and stability of CaO catalyst can be enhanced by doping with KCl. Lee et al. [9] also proved that the binary MgO–ZnO catalyst exhibits superior physicochemical properties as compared to MgO or ZnO catalysts.

Barium oxide catalysts were reported to exhibit superior catalytic performance in transesterification. The catalytic reactivity of BaO is higher than CaO, SrO and MgO due to its high basicity [11–16]. The catalytic properties of BaO supported on Al₂O₃ [17], SiO₂ [18] and SrO(Al₂O₃) [19] towards the transesterification reaction have also been studied. The reactivity of the supported BaO catalysts can be related to its dispersion on the support, surface composition and surface properties. Thus far, the study on barium-based binary or tertiary oxides in transesterification is rarely reported. The only two recent studies were conducted by Sherstyuk et al. [20, 21]. They successfully prepared Ba–Al–O (viz. BaAl_{13.2}O_{20.8} and BaAl₁₂O₁₉) and Ba–La–O (viz. BaLa₂O₄/La₂O₃ and Ba_{0.04}La_{1.96}O₃) binary systems via precipitation and calcination method and demonstrated their application in the transesterification of

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rapeseed oil. The stability of Ba–Al–O is higher than Ba–La–O binary catalysts and the conversion of rapeseed oil over Ba–Al–O can achieve $\sim 100\%$ at optimum conditions.

Recently, we have successfully synthesized BaTiO₃, Na-doped BaTiO₃ [22] and Ba₂NiTi₅O₁₃ [23] particles via sol–gel and calcination method. As the continuation of the work, herewith, we report their catalytic study in the transesterification of palm cooking oil. The Na-doped Ba₂NiTi₅O₁₃ was also prepared for comparison purposes. The surface properties of un-doped and doped oxides are studied via SEM, BET and benzoic acid titration. The influence of sodium dopant on the surface properties, as well as the catalytic performance is also reported in this study.

Materials and methods

Materials

All materials were used as purchased. Titanium tetraisopropoxide (Ti(OPrⁱ)₄, 99.999%, Fluka), barium hydroxide monohydrate (Ba(OH)₂·H₂O, $\geq 98\%$, Fluka), nickel acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O, $\geq 99.0\%$, Fluka), sodium hydroxide (NaOH, $\geq 99.99\%$, JT Baker), sodium carbonate (NaCO₃, $\geq 99.5\%$, R&M), methanol (CH₃OH; $\geq 98\%$, R&M Chemicals), isopropanol ((CH₃)₂CHOH, $\geq 99.7\%$, R&M Chemicals), *n*-hexane (C₆H₁₄, $\geq 99\%$, QR&C), benzoic acid (C₆H₅COOH, $\geq 99.5\%$, Sigma Aldrich) and acetic acid (CH₃COOH, $\geq 99.8\%$, Systerm) were analytical grade. Palm cooking oil (Delima Oil Products Sdn. Bhd) was obtained commercially.

Preparation of catalysts

In general, the catalysts were prepared via sol–gel method followed by calcination. Detailed description on the preparation of BaTiO₃, Na-doped BaTiO₃ and Ba₂NiTi₅O₁₃ has been reported elsewhere [22, 23].

BaTiO₃ and sodium doped BaTiO₃ (Na-BaTiO₃)

As much as 399.7 mg of Ba(OH)₂·H₂O was dissolved in 40 mL of distilled water heated in an oil bath at 50 °C. Then, 8 mL of 0.044 M of Ti(OPrⁱ)₄ in isopropanol (molar ratio of Ba:Ti = 6:1) was then added. The mixture was stirred for 2 h under reflux. The product (in gel form) was separated via centrifugation and washed with distilled water. The BaTiO₃ catalyst was obtained by calcination of the gel at 900 °C for an hour. The 0.5 mol% sodium doped derivatives was similarly prepared. However, the stipulated NaCO₃ was added to Ba(OH)₂·H₂O before the addition of

Ti(OPrⁱ)₄. The obtained gel was then calcined at 900 °C for 5 h.

Ba₂NiTi₅O₁₃ and sodium doped Ba₂NiTi₅O₁₃ (Na-Ba₂NiTi₅O₁₃)

Typically, the Ba₂NiTi₅O₁₃ was synthesized via two-steps. As much as 5×10^{-3} mol of Ni(CH₃COO)₂·4H₂O was dissolved in a mixture of isopropanol/acetic acid. Then, 1.5 mL of 3.33 M Ti(OPrⁱ)₄ was added (at a mole ratio of Ni:Ti = 1:1). The mixture was stirred at room temperature for 24 h until an olive green solution was formed. As much as 50 mL of distilled water was then added before subjecting to partial freeze-drying process. The obtained product (as-prepared NiTiO₃ gel) was used in the subsequent step.

In a separate flask, 799.4 mg of Ba(OH)₂·H₂O was dissolved in 80 mL of distilled water and mixed with 32 mL of 3.0 M NaOH. The whole system was heated at 50 °C while stirring to ensure the total dissolution. Then, 652.8 mg of the as-prepared gel obtained previously was added. This was followed by the addition of 16 mL of 0.044 M Ti(OPrⁱ)₄ in isopropanol. The mole ratio of Ba:Ni:Ti was fixed at 1:1:1.2. The mixture was stirred for another 8 h. The product (in gel form) was separated via centrifugation and washed with distilled water. The Ba₂NiTi₅O₁₃ catalyst was obtained by the calcination of gel product at 900 °C for 8 h. The sodium doped derivatives (viz. 0.5 mol% Na) were similarly prepared. However, the stipulated NaCO₃ was added before addition of Ti(OPrⁱ)₄ in the second step. The obtained gel product was then calcined at 900 °C for 5 h.

Characterizations

The surface structures and average size of the catalysts were determined by scanning electron microscope (SEM) equipped with electron energy dispersive X-ray spectroscopy (EDX) performed on a Leica Cambridge Stereoscan S360 operating at 15 kV. The surface area and porosity of the catalysts were examined using a Micromeritics ASAP 2000. Samples were degassed at 160 °C prior to isotherm analysis. Branauer–Emmett–Teller (BET) isotherm was performed by adsorption of nitrogen at −196 °C. The surface area was then calculated using BET equation. The basicity analyses of the respective catalysts were determined by benzoic acid titration using the following indicators: bromothymol blue ($H_L = 7.2$), phenolphthalein ($H_L = 8.2$ – 9.8), 2,4-dinitroaniline ($H_L = 15.0$) and 4-nitroaniline ($H_L = 18.4$) [24, 25].



Transesterification reaction

Transesterification reaction was carried out by heating a mixture of palm cooking oil, methanol and the as-prepared catalyst in an autoclave at the desired temperature and duration. The BaTiO₃ catalyst was employed to study the reaction optimization for the series of catalysts investigated. The four parameters: reaction temperatures (80–180 °C), duration (0.5–6.0 h), ratios of oil to methanol (1:3–1:15 v/v) and catalyst loading (0.5–10.0 wt/v% referred to the initial palm oil volume) were investigated to determine the optimum reaction conditions.

After the transesterification reaction, the mixture was allowed to cool down before separating the methyl ester (ME) by centrifugation. The products were weighed and analyzed using an Agilent 7890A gas chromatography (GC) fitted with a flame ionization detector (FID). The % of ME yield was calculated using the following equation [26]:

$$\begin{aligned} & \% \text{ Methyl esters yield} \\ &= \frac{\text{Total ME areas from GC} \times \text{weight of product}}{\text{Weight of cooking oil}} \times 100\% \end{aligned} \quad (1)$$

Results and discussions

Surface characterizations

The typical morphological structures of un-doped and doped oxides are depicted in Fig. 1. All the samples show porous aggregates which were made up of distinct particles. These particles are mostly nearly spherical to cube in shape. The average particle size of the prepared BaTiO₃ and Ba₂NiTi₅O₁₃ are 140.0 ± 31.0 and 89.4 ± 32.2 nm, respectively. These values increased to 240.0 ± 68.0 and 125.1 ± 30.5 nm for the respective oxides upon Na doping. The surface areas and pore sizes of the samples were characterized by BET analysis and are presented in Table 1. The prepared BaTiO₃ and Ba₂NiTi₅O₁₃ exhibited a surface area of about 3.0 and 3.8 m² g⁻¹, respectively. Na doping decreased the surface area (and therefore the pore size) of the oxides. For instance, the respective surface area for Na-BaTiO₃ and Na-Ba₂NiTi₅O₁₃ was 2.6 and 2.8 m² g⁻¹.

Several studies [27, 28] have shown that doping constrains the growth of oxide particles and thus smaller particles with higher surface area are obtained. However, this study shows otherwise, i.e., increment in the average particle size and a decrement in surface area and pore size upon Na doping. This may be attributed to the formation of

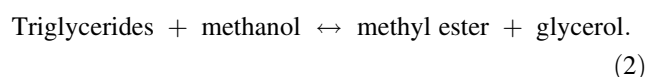
a dense layer of Na secondary phase on the oxides and plugged the pores. XRD analyses (not shown) have confirmed the formation of Na_{1.7}Ba_{0.45}Ti_{5.85}O₁₃ and NaBa₂NiTi₅O₁₃ on the respective outermost surface of the BaTiO₃ and Ba₂NiTi₅O₁₃ [22, 23].

As seen in Table 2, BaTiO₃ and Ba₂NiTi₅O₁₃ exert a total basicity of 0.540 and 0.618 mmol g⁻¹, respectively. Most of the basic sites of these oxides are in the range of 7.2 < H₊ < 8.2 (weaker basic sites). It covers ~54% of the total basic sites. The total basicity of the oxides increased almost twofold upon Na doping. This was 1.062 and 1.336 mmol g⁻¹ for Na-BaTiO₃ and Na-Ba₂NiTi₅O₁₃, respectively. The percentage of medium basic sites in Na-Ba₂NiTi₅O₁₃ is higher as compared to Na-BaTiO₃. The Na-BaTiO₃ possess 13.0% while Na-Ba₂NiTi₅O₁₃ offers 20.4% basic sites in the range of 15.0 < H₊ < 18.4.

Optimization of transesterification

The catalytic activities of BaTiO₃ at various reaction parameters were compared to obtain the optimum reaction conditions. As seen in Table 3, the percentage of ME yield increases with the increase in the ratio of oil:methanol up to 1:12 (v/v), and thereafter ME yield decreases. For instance, the ME yield for the oil:methanol ratio of 1:3 (v/v) is 82.3%. This increases to 86.5 and 88.1% upon further increase in the oil:methanol volume ratio to 1:9 (v/v) and 1:12 (v/v) correspondingly. Further increase in the content of methanol to 1:15 (v/v) caused the ME yield to drop to 78.8%.

Palm oil transesterification is a reversible reaction (Eq. 2). Hence, forward reaction is favored in an excess amount of methanol, i.e., from 1:3 to 1:12 (v/v) oil:methanol. However, at high methanol ratio (in the 1:15 (v/v) oil to methanol), the dilution effect becomes prominent. This caused a reduction in reaction rate, hence a lower ME yield is obtained [29]. In addition, large amount of methanol can also promote the solubility of glycerol in the oil and can cause difficulty in the separation of glycerol [30]. Therefore, the ratio of oil to methanol of 1:12 (v/v) is chosen for this transesterification study.



The catalyst loading is another factor that affects the ME yield. Typically, increasing the loading amount of catalysts may provide more catalytic sites for reactants to dock on. In this study, it is observed that the % of ME yield increases gradually from 0.5 to 10 wt/v% catalyst loading. The ME yield was 78.2, 84.5, 88.1 and 88.8% for the 0.5, 2.0, 5.0 and 10.0 wt/v% BaTiO₃ loading, respectively. The



Fig. 1 Typical SEM micrographs of **a** BaTiO₃, **b** Na-BaTiO₃, **c** Ba₂NiTi₅O₁₃ and **d** Na-Ba₂NiTi₅O₁₃

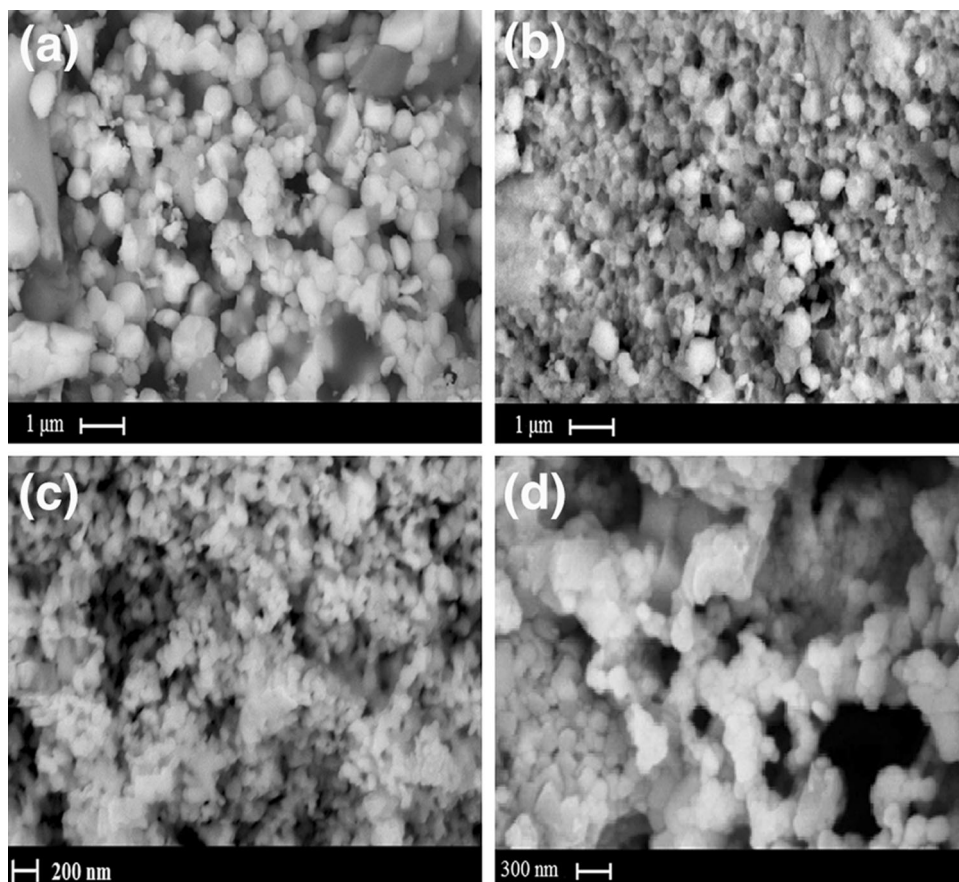


Table 1 Surface characteristics of various barium-containing catalysts

Catalyst	Surface area (m ² g ⁻¹)	Pore size (nm)	Particle size (nm)
BaTiO ₃	3.0	30.5	140.0 ± 31.0
Na-BaTiO ₃	2.6	21.7	240.0 ± 68.0
Ba ₂ NiTi ₅ O ₁₃	3.8	39.5	89.4 ± 32.2
Na-Ba ₂ NiTi ₅ O ₁₃	2.8	30.8	125.1 ± 30.5

Table 2 Basicity of various oxides and their Na-doped counterparts

Catalyst	Basicity (mmol g ⁻¹)				Total basicity (mmol g ⁻¹)
	H ₊ = 7.2	H ₊ = 8.2–9.8	H ₊ = 15.0	H ₊ = 18.4	
BaTiO ₃	0.29	0.15	0.10	0	0.540
Na-BaTiO ₃	0.74	0.19	0.14	0	1.062
Ba ₂ NiTi ₅ O ₁₃	0.33	0.17	0.12	0	0.618
Na-Ba ₂ NiTi ₅ O ₁₃	0.90	0.16	0.27	0	1.336

% yield for the 5 and 10 wt/v% catalyst is similar. Accordingly, the 5 wt/v% catalyst was chosen as the optimum amount for further studies.

An increment of ME yield from 76.0 to 88.1% is achieved via increasing the reaction temperature from 80 to 150 °C. Beyond 150 °C, the ME yield is constant. Generally, increasing temperature helps in homogenizing the reactants, making them more readily to react [31]. Hence,

this may assist the transesterification to reach equilibrium faster, and thus affects the % of ME yield for transesterification.

As shown in Table 3, the % of ME yield increases from 74.8 to 88.1% when increasing the time duration from 0.5 to 2 h. After that, the reaction yield is more or less constant (~90–92%). Hence, it is envisaged that 2 h is sufficient to complete the reaction.



Table 3 Methyl ester conversion of the BaTiO₃ catalyst at various conditions

Parameters					% ME yield
	Ratio of oil:CH ₃ OH (v/v)	Temperature (°C)	Duration (h)	Catalyst loading (wt/v%)	
	1:3	150	2.0	5.0	82.3
	1:6	150	2.0	5.0	86.4
	1:9	150	2.0	5.0	86.5
	1:12	150	2.0	5.0	88.1
	1:15	150	2.0	5.0	78.8
	1:12	150	2.0	0.5	78.2
	1:12	150	2.0	1.0	84.4
	1:12	150	2.0	2.0	84.5
	1:12	150	2.0	10.0	88.8
	1:12	150	0.5	5.0	74.8
	1:12	150	1.0	5.0	79.5
	1:12	150	3.0	5.0	90.8
	1:12	150	4.0	5.0	91.3
	1:12	150	5.0	5.0	92.0
	1:12	150	6.0	5.0	92.1
	1:12	80	2.0	5.0	76.0
	1:12	100	2.0	5.0	80.8
	1:12	120	2.0	5.0	82.3
	1:12	180	2.0	5.0	88.2

Transesterification of palm cooking oil

As shown in Table 2, BaTiO₃ demonstrated 88% of ME yield. Ba₂NiTi₅O₁₃ gave a higher ME value of 91% as compared to BaTiO₃. These values increased 2–6% upon doping 0.5 wt% Na into the respective oxide catalysts. The catalytic activity of barium-containing catalysts follows the trend of decreasing order of Na-Ba₂NiTi₅O₁₃ > Ba₂NiTi₅O₁₃ > Na-BaTiO₃ > BaTiO₃.

In general, the catalytic properties are influenced by particle size, surface area, as well as the active sites of a catalyst. Small sized catalyst with high surface area and active sites will give rise to high catalytic performance. In this study, however, the sizes and surface areas seem to contribute to only minor extent towards transesterification. Instead, the catalytic performance of the series of un-doped and doped barium-containing titanate catalysts is believed to be closely related to their basic sites. For instance, the Na-Ba₂NiTi₅O₁₃ which the highest amount of medium basic sites displayed the highest catalytic activity. However, the Na-BaTiO₃ with the smallest average particle size gave lower catalytic activity even though it offers the highest surface area among the series. A similar finding was reported by Nascimento et al. [32]. As previously mentioned [22, 23], a dense layer of Na secondary phase was formed onto the surface of barium-containing titanate catalysts in the Na-doped system. There are 50% more basic sites located on these Na secondary phase as

compared to un-doped system. These sites are actively involved in the adsorption of methanol in which the O–H bonds of the methanol readily break into methoxides and proton [33]. The methoxides formed then reacted with the triglyceride to yield methyl esters and glycerols. The proposed mechanism is depicted in Fig. 2.

Table 4 also shows a comparison of catalytic activity between this work and other barium-containing catalyst systems. As can be seen, the ME yield (88–95%) obtained in this work are comparable to the previous reported values. The highest ME yield achieved in the literature was 100% for the Ba_{0.04}La_{1.96}O₃ catalyst using rapeseed oil as the feed stock. Nevertheless, higher catalyst loading and temperature, as well as a longer reaction time were needed as compared to this study.

Conclusion

BaTiO₃, Ba₂NiTi₅O₁₃ and their Na-doped analogues were successfully synthesized via sol–gel and calcination method. The prepared BaTiO₃ and Ba₂NiTi₅O₁₃ exert porous aggregated structure with specific surface area of 3–4 m² g^{−1}. They displayed a total basicity of 0.5–0.6 mmol g^{−1} with ~81% of weak basic sites. Doping these oxides with Na increased their total basicity (i.e., to 1.1–1.3 mmol g^{−1}) but decreased their surface area and pore size. This may be attributed to the formation of a dense



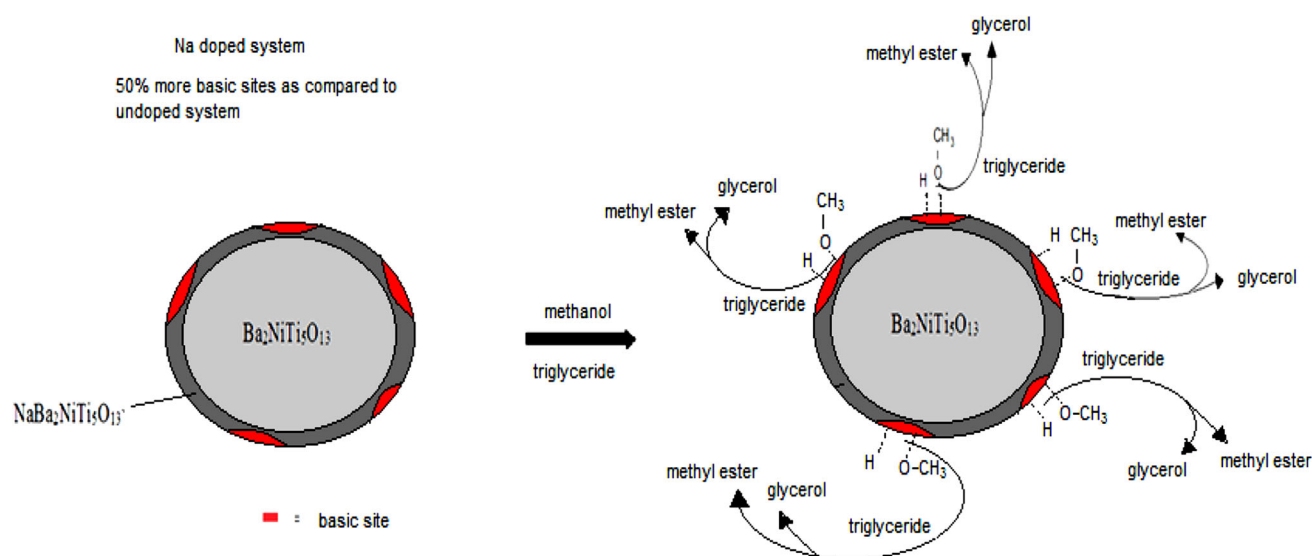


Fig. 2 Proposed mechanism for the beneficial effect of adding Na onto the barium-containing titanate catalysts

Table 4 Comparison of catalytic performance of various barium-containing catalysts in the literature

Catalyst	Type of oil	Reaction condition				ME (%)	Ref.
		Loading (wt%)	Methanol:oil ratio(v/v)	Temperature (°C)	Duration (min)		
BaZrO ₃	Keranja	1	27:1	65	180	99	[34]
Ba-MMT	Waste cooking	3.5	12:1	150	300	83	[7]
Ba(OH) ₂	Corn	3.6	11.32:1	33	118	99	[35]
Ba-Sr/ZSM-5	Sunflower	3	9:1	60	180	88	[36]
Ba _{0.04} La _{1.96} O ₃	Rapeseed	6	9:1	200	540	100	[20]
BaAl ₁₂ O ₁₉	Rapeseed	2	9:1	200	540	60	[20]
Na-Ba ₂ NiTi ₅ O ₁₃	Palm	5	15:1	150	120	95	This study
Ba ₂ NiTi ₅ O ₁₃	Palm	5	15:1	150	120	91	This study
Na-BaTiO ₃	Palm	5	15:1	150	120	90	This study
BaTiO ₃	Palm	5	15:1	150	120	88	This study

layer of Na secondary phase on the oxides that plugged the pores. The optimum conditions for the transesterification were obtained with 5 wt/v% catalysts loading at oil to methanol ratio of 1:12 (v/v) and at 150 °C for 2 h. Both undoped and doped BaTiO₃ and Ba₂NiTi₅O₁₃ showed good catalytic activity towards the transesterification of palm cooking oil with more than 85% conversion. The catalytic activity of barium-containing titanate catalysts follows the trend of decreasing order of Na-Ba₂NiTi₅O₁₃ > Ba₂NiTi₅O₁₃ > Na-BaTiO₃ > BaTiO₃. The catalytic performance of these series of un-doped and doped barium-containing catalysts is believed to be closely related to their surface basic sites but not the total surface area.

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References

1. Sajjada, B., Abdul Rahman, A.A., Arandiyah, H.: A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: composition, specifications and prediction models. *Renew Sust Energy Rev* **63**, 62–92 (2016)
2. Demirbas, A.: *Biodiesel: a realistic fuel alternative for diesel engines*. Springer, London (2007)
3. Leung, D.Y.C., Wu, X., Leung, M.K.H.: A review on biodiesel production using catalyzed transesterification. *Appl Energy* **87**, 1083–1095 (2010)



4. Avhad, M.R., Marchetti, J.M.: Innovation in solid heterogeneous catalysis for the generation of economically viable and eco-friendly biodiesel: a review. *Catal Rev Sci Eng* **58**, 157–208 (2016)
5. Chorkendoff, I., Niemantsverdriet, J.W.: Concepts of modern catalysis and kinetic. Wiley, Weinheim (2003)
6. Mar, W., Samsook, E.: Methanolysis of soybean oil over KCl/CaO solid base catalyst for biodiesel production. *Sci Asia* **38**, 90–94 (2012)
7. Olutoye, M.A., Wong, S.W., Chin, L.H., Amani, H., Asif, M., Hameed, B.H.: Synthesis of fatty acid methyl esters via the transesterification of waste cooking oil by methanol with a barium-modified montmorillonite K10 catalyst. *Renew Energy* **86**, 392–398 (2016)
8. Mukenga, M., Muzenda, E., Jalama, K., Mijiboom, R.: Biodiesel production from soybean oil over TiO₂ supported nano-ZnO. *Int J Chem Nucl Mater Metall Eng* **6**, 348–352 (2012)
9. Lee, H.V., Taufiq-Yap, Y.H., Hussein, M.Z., Yunus, R.: Transesterification of jatropha oil with methanol over Mg–Zn mixed metal oxide catalysts. *Energy* **49**, 12–18 (2013)
10. Fan, M., Liu, Y., Zhang, P., Jiang, P.: Blocky shapes Ca–Mg mixed oxides as a water-resistant catalyst for effective synthesis of biodiesel by transesterification. *Fuel Process Technol* **149**, 163–168 (2016)
11. Gotcht, A.J., Reeder, A.J., McCormick, A.: Study of heterogeneous base catalysts for biodiesel production. *J Undergrad Chem Res* **8**, 22–26 (2009)
12. Patil, P., Gude, V.G., Pinappu, S., Deng, S.: Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under conventional and microwave heating conditions. *Chem Eng J* **168**, 1296–1300 (2011)
13. Babak, S., Iman, H., Abdullah, A.Z.: Alkaline earth metal oxide catalysts for biodiesel production from palm oil: elucidation of process behaviors and modeling using response surface methodology. *Iran J Chem Chem Eng* **32**, 113–126 (2013)
14. Mootabadi, H., Salamatinia, B., Bhatia, S., Abdullah, A.Z.: Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. *Fuel* **89**, 1818–1825 (2010)
15. Patil, P.D., Gude, V.G., Deng, S.: Biodiesel production from Jatropha Curacas, waste cooking and Camelina Sativa Oils. *Ind Eng Chem Res* **48**, 10850–10856 (2009)
16. Martinez-Guerra, E., Gude, V.G.: Transesterification of used vegetable oil catalyzed by barium oxide under simultaneous microwave and ultrasound irradiations. *Energy Convers Manag* **88**, 633–640 (2014)
17. Anderson, J.A., Beaton, A., Galadima, A., Wells, R.P.K.: Role of Baria dispersion in BaO/Al₂O₃ catalysts for transesterification. *Catal Lett* **131**, 213–218 (2009)
18. Sullivan, J.A., Sherry, L.: Different dispersions of group II catalysts over SBA-15 and MCM-41: effects on transesterification reactivity. *Catal Comm* **60**, 88–91 (2015)
19. Mierczynski, P., Ciesielski, R., Kedziora, A., Maniukiewicz, W., Shtyka, O., Kubicki, J., Albinska, J., Maniecki, T.P.: Biodiesel production on MgO, CaO, SrO and BaO oxides supported on (SrO)(Al₂O₃) mixed oxide. *Catal Lett* **145**, 1196–1205 (2015)
20. Sherstyuk, O.V., Ivanova, A.S., Lebedev, M.Y., Bukhtiyarova, M.V., Matvienko, L.G., Budneva, A.A., Simonov, A.N., Yakovlev, V.A.: Transesterification of rapeseed oil under flow conditions catalyzed by basic solids: M–Al(La)–O (M=Sr, Ba), M–Mg–O (M=Y, La). *Appl Catal A Gener* **419–420**, 73–83 (2012)
21. Ivanova, A.S., Sherstyuk, O.V., Bukhtiyarova, M.V., Kukushkin, R.G., Matvienko, L.G., Plyasova, L.M., Kaichev, V.V., Simonov, A.N., Yakovlev, V.A.: Performance of Ba-containing catalysts in the transesterification reaction of rapeseed oil with methanol under flow conditions. *Catal Comm* **18**, 156–160 (2012)
22. Chew, K.Y., Abu Bakar, M., Abu Bakar, N.H.H.: Effects of sodium doping on phase composition and morphology of barium titanate particles. *AIP Conf Proc* **1502**, 348–367 (2012)
23. Chew, K.Y., Abu Bakar, M.: Two steps synthesis of quaternary metal titanate of Ba₂NiTi₅O₁₃ and characterization. *Adv Mater Res* **364**, 353–358 (2012)
24. Markowitz, M.A., Schoen, P.E., Kust, P., Gaber, B.P.: Surface acidity and basicity of functionalized silica particles. *Colloids Surf A* **150**, 85–94 (1999)
25. Van Laar, F.M.P.R., De Vos, D.E., Pierard, F., Kirsch-De Mesmaeker, A., Fiermans, L., Jacobs, P.A.: Generation of singlet molecular oxygen from H₂O₂ with molybdate-exchanged layered double hydroxides: effects of catalyst composition and reaction conditions. *J Catal* **197**, 139–150 (2001)
26. Omar, Wan: W.N.N., Amin, N.A.S.: Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Process. Technol.* **92**, 2397–2405 (2011)
27. Hinojosa-Reyes, M., Arriaga, S., Diaz-Torres, L.A., Rodríguez-González, V.: Gas-phase photocatalytic decomposition of ethylbenzene over perlite granules coated with indium doped TiO₂. *Chem Eng J* **224**, 106–113 (2013)
28. Li, Y., Li, J., Li, Q., Yu, G.-L., Zhang, H.-W.: Structure and magnetic properties of NiCuZn ferrite materials with La doping. *Rare Met* (2013). doi:[10.1007/s12598-014-0376-2](https://doi.org/10.1007/s12598-014-0376-2)
29. Gao, L., Xu, B., Xiao, G., Lu, J.: Transesterification of palm oil with methanol to biodiesel over a KF/hydrotalcite solid catalyst. *Energy Fuels* **22**, 3531–3535 (2008)
30. Meher, L.C., Kulkarni, M.G., Dalai, A.K., Naik, S.N.: Transesterification of karanja (*Pongamia pinnata*) oil by solid basic catalysts. *Eur J Lipid Sci Technol* **108**, 389–397 (2006)
31. Nguyen, T., Do, L., Sabatini, D.A.: Biodiesel production via peanut oil extraction using diesel-based reverse-micellar microemulsions. *Fuel* **89**, 2285–2291 (2010)
32. Nascimento, G.S., Mambrini, G.P., Paris, E.C., Peres, J.A., Colnago, L.A., Ribeiro, C.: Evaluation of the catalytic activity of oxide nanoparticles synthesized by the polymeric precursor method on biodiesel production. *J Mater Res* **27**, 3020–3026 (2012)
33. Refaat, A.A.: Biodiesel production using solid metal oxide catalysts. *Int J Environ Sci Technol* **8**, 203–221 (2011)
34. Singh, V., Hameed, B.H., Sharma, Y.C.: Economically viable production of biodiesel from a rural feedstock from eastern India, *P. pinnata* oil using a recyclable laboratory synthesized heterogeneous catalyst. *Energy Convers Manag* **122**, 52–62 (2016)
35. Mustafa, F., Bicu, I.: The optimization of the production of methyl esters from corn oil using barium hydroxide as a heterogeneous catalyst. *J Am Oil Chem Soc* **91**, 839–847 (2014)
36. Feyzi, M., Khajavi, G.: Investigation of biodiesel production using modified strontium nanocatalysts supported on the ZSM-5 zeolite. *Ind Crops Prod* **58**, 298–304 (2014)

